

Formation and Extraction of Persistent Fumigant Residues in Soils

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Fumigants are commonly thought to be short-lived in soil, but residues have been found in soils years following application. In this study, formation and extraction of persistent soil fumigant residues were investigated. Fumigants 1,3-dichloropropene (1,3-D), chloropicrin (CP), and methyl isothiocyanate (MITC) were spiked into Arlington, Glenelg, and Hagerstown soils and incubated for 30 d under controlled conditions. The incubated soils were evaporated for 20 h prior to extraction with a variety of organic solvents at different temperatures. Extraction with acetonitrile in sealed vials at 80 °C for 24 h was the most efficient method to recover persistent soil fumigant residues. At application rates of 1000–1700 mg (kg of soil)⁻¹, persistent residues of 1,3-D, CP, and MITC in the three soils ranged from 5 to 67 mg kg⁻¹. The residue content increased with application rate, correlated positively with soil silt content, decreased dramatically as indigenous organic matter (OM) was removed, and changed little with external OM addition. Adsorption to clay surfaces was not important in fumigant retention, while pulverization of soil aggregates significantly decreased persistent fumigant residues. The results suggest that persistent fumigant residues are retained in soil intra-aggregate micropores resulting from binding clay flocs and silt particles by humic substances.

Introduction

Fumigants are a variety of biocides used to control weeds, pathogens, nematodes, and soil fungi by fumigation. These types of pesticides have high vapor pressures at room temperature and become fumes rapidly in open systems. Once applied to the field, fumigants quickly disperse in soils through gas-phase diffusion, and the soil disinfestation effect is achieved.

The environmental fate of field-applied fumigants is of great concern because of their impacts on environmental quality and human health. It is commonly believed that dissipation of soil fumigants is mainly through three pathways: volatilization to the atmosphere, degradation via chemical reactions, and decomposition by microbial activities (1, 2). Because of the high volatility, low sorptivity, and rapid degradation rate of fumigants in soils, persistent soil fumigant

residues are usually considered insignificant, especially long after application. However, Steinberg et al. (3) observed that fumigant 1,2-dibromoethane (EDB) persisted in soils for a number of years following application. Pignatello (4) incubated a sandy loam soil with fumigant 1,2-dichloropropene (DCP) at 10 mg g⁻¹ for 57 d and then spread the soil in a thin layer and evaporated it for 3 h in a fume hood, and 4.9 mg kg⁻¹ of DCP was detected remaining in the evaporated soil. Tao and Maciel (5) reported that methyl bromide (MeBr) remained in fumigated soil for over 1 week in open systems. Evidently, persistent fumigant residues in treated soils may be significant.

The persistent fumigant residue in soil has great environmental implications. In addition to potential impacts on soil microbial communities, slow release of the residue may contaminate groundwater. For instance, 1,3-dichloropropene (1,3-D), an important fumigant, has been detected in groundwater in many states (6), and the U.S. Environmental Protection Agency has listed it as a drinking water contaminant candidate (7). Other fumigants such as EDB, DCP, MeBr, and 1,2-dibromo-3-chloropropene (DBCP) were also detected in groundwater and aquifers (8).

Despite the substantial existence and environmental significance of persistent soil fumigant residues, this topic has not drawn much attention. Mechanisms for the residue formation are poorly understood, and effects of environmental factors are unclear. Furthermore, effective yet simple extraction methods for persistent soil fumigant residues are not available. With batch sorption techniques conducted by spiking aqueous halogenated aliphatic hydrocarbons (HHCs, including fumigants) into 1:1 soil–water suspensions, Pignatello (4) observed that the weakly sorbing chemicals formed slowly reversible residues in soils and the residues became greater in magnitude and less mobile as the equilibrium time increased. Since fumigants are usually injected directly into moist soil, the results need to be confirmed for practical conditions. In a related study, the same author found that HHC residues correlated with organic carbon contents in whole soils or separated particle fractions and proposed that the residue formation was principally via molecular diffusion into soil organic matter matrix and minerals had little contribution (9). The effect of organic matter amendment, temperature, moisture, soil aggregation, and other factors that affect molecular diffusion on the formation of fumigant residues has yet to be determined.

Fumigants are commonly extracted from soil with ethyl acetate at room temperature for 1 h (10). The routine extraction has a good recovery (i.e., 95%) for soils freshly spiked with fumigants, but it is ineffective for field samples (11). Sawhney et al. (11) evaluated various methods to extract residual EDB in field soils and found that extraction of a fumigated sandy loam soil with methanol (1:5 mass/volume ratio) at 75 °C for 24 h in a sealed vial gave the highest recovery, while Soxhlet extraction, sonication extraction and purge-and-trap methods yielded considerably lower recoveries. The suggested method is simple and convenient, but needs to be validated for other soils and fumigants.

In this study, the effect of environmental factors such as application rate, reaction time, soil moisture, temperature, texture, aggregation, mineralogy, and organic matter on the formation of persistent residues of fumigants 1,3-D, methyl isothiocyanate (MITC), and chloropicrin (CP) in three types of soils was investigated. Thermal extraction techniques with different solvents, extraction time, and temperature for persistent fumigant residues were optimized. The three chemicals are widely applied fumigants, but the persistent

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TABLE 1. Selected Physical and Chemical Properties of Soils

soil	clay (%)	silt (%)	sand (%)	OC (g kg ⁻¹)	pH
Arlington	7.4	18.0	74.6	9.2	7.2
Glenelg	27.6	45.5	26.9	25.9	7.3
Hagerstown	26.9	65.1	8.0	14.4	5.9

residue formation in soil and extraction have not been reported in the literature.

Materials and Methods

Chemicals and Soils. Three fumigants were included in this study: 1,3-D, MITC, and CP. The 1,3-D was provided by Dow Agrosiences Company (Indianapolis, IN), and it contained 50.3% *cis*- and 47.5% *trans*-isomers. The MITC (purity 99.9%) was purchased from Chem Service Co. (West Chester, PA), and CP (purity 99.9%) was provided by Niklor Chemical Co. (Long Beach, CA).

Three soils were collected in California and Pennsylvania: an Arlington sandy loam soil (coarse-loamy, mixed, thermic Haplic Durixeralfs) from the University of California Agricultural Experiment Station in Riverside, CA; a Glenelg channery loam soil (fine-loamy, mixed, semiactive, mesic Typic Hapludalts) from a grassland in West Grove, PA; and a Hagerstown silt loam soil (fine, mixed, semiactive, mesic Typic Hapludalts) sampled from a farmland in University Park, PA. The sampling sites had never been treated with any fumigants. The soils were air-dried, passed through a 2-mm sieve, and stored at 20 ± 1 °C prior to use. Selected physical and chemical properties of the soils are given in Table 1.

Incubation Experiments. Air-dried soils were adjusted to 10% moisture content and mixed well, and aliquots of 10 g (oven dry mass) were weighed into 20-mL glass vials. The vials were capped with aluminum covers and Teflon-faced butyl rubber septa. Ten microliters of 1,3-D or CP was then injected into the vials with a 10-μL microsyringe. For MITC, 10 mg of the chemical was weighed into each vial in a fume hood with a 4-digit balance, and the vials were recapped immediately. The application rates of 1,3-D, CP, and MITC were 1190, 1690, and 1000 mg (kg of soil)⁻¹, respectively, which are greater than would be encountered in actual field applications. Formation of persistent fumigant residues at lower application rates (10–169 mg (kg of soil)⁻¹) was also investigated. To ensure satisfactory sealing effects, the vial heads were dipped into melted paraffin wax. The vials were incubated in the dark at 20 ± 1 °C for 30 d without disturbance.

Samples for persistent residue extraction optimization were prepared by amending Arlington soil with a Florida organic soil (collected from Belle Glade, FL; pH 7.2, organic carbon [OC] content 460 g kg⁻¹) to OC 30.7 g kg⁻¹ and incubating the fumigated soil (spiked as described above, moisture content 10%) at 20 °C for 30 d. To study persistent soil fumigant residue formation and the effect of environmental factors, fumigant-spiked soils were incubated under particular conditions. Effects of application rate and multi-fumigant interactions were investigated by spiking 1,3-D, CP, and MITC separately and together into soils (10% moisture content, same as follows if not specified) at various rates from <35 to >1000 mg kg⁻¹. The effect of temperature was determined by incubating fumigant-spiked soils at 20, 35, and 50 ± 1 °C, respectively. Samples incubated at 20 °C were withdrawn at specified times to investigate the effect of incubation duration. For the moisture effect, air-dried soils were adjusted to water content <1% (air-dried), 5%, 10%, 15%, and 20%; spiked with fumigants; and incubated at 20 ± 1 °C for 30 d. For the particle size effect, acid-washed quartz sand was ground and sieved to obtain coarse (1–2 mm), medium (0.1–0.25 mm), and fine (<0.075 mm) size

fractions and treated as described above. To study the soil aggregation effect, air-dried Arlington soil (<2 mm) was ground to completely pass through a 0.25- or 0.075-mm sieve, and the pulverized soils were incubated with fumigants. The effect of organic matter (OM) was examined by heating the three soils at 375 °C for 10 h to remove OM and incubating the OM-free soils with fumigants at 20 ± 1 °C for 30 d. The heating condition would remove OM completely while alter little of soil texture and mineralogical composition (12). Arlington soil was amended to OC 22.3 and 34.7 g kg⁻¹ with the organic soil and incubated with fumigants at 20 °C. Furthermore, Na⁺-montmorillonite (Clay Minerals Repository, University of Missouri, Columbia, MO), Na⁺-kaolinite (Ward's Natural Science Establishment Inc., Rochester, NY), and hematite (Fisher Scientific, Fair Lawn, NJ) were adjusted to 20% water content, spiked with fumigants, and incubated at 20 ± 1 °C for 30 d to test clay and mineralogy effects.

Persistent Residue Extraction. After being incubated, soils were spread into a thin layer on aluminum foil in a fume hood, allowing evaporation for 20 h. The evaporated soils were then put back into their original vials, and 1 g of anhydrous sodium sulfate (to absorb water) and 10 mL of solvent were added. The vials were sealed with aluminum covers and Teflon-faced rubber septa and extracted at a preset temperature for a determined time period.

To develop an effective extraction method, different extraction solvents, temperatures, and durations were tested. Test organic solvents were acetone, acetonitrile, ethyl acetate, hexane, and methanol, and test temperatures were 20, 50, and 80 °C. Extraction times were 1, 12, and 24 h. Samples extracted at 20 °C were shaken continuously, while those at 50 °C (in an incubator) and at 80 °C (in a water bath) were mixed occasionally. Soil to solvent ratio (mass/volume) and multi-round extraction were also evaluated after the most efficient solvent, temperature, and time were determined, and an optimized extraction method was eventually obtained.

The optimized extraction method was then used to extract persistent fumigant residues from soils incubated under particular conditions. Effects of various environmental factors on the formation of persistent fumigant residues were examined.

Chemical Analysis. After being extracted, the suspensions were centrifuged at 956g for 15 min, and the supernatants were carefully pipetted into 2-mL GC vials for fumigant analysis with a HP6890 GC system (Hewlett-Packard, Avondale, PA) consisting of an electron capture detector (for 1,3-D and CP), a nitrogen phosphorus detector (for MITC), and a RTX-624 capillary column (30 m long × 0.25 mm i.d. × 1.4 μm film thickness; Restek Co., Bellefonte, PA). The carrier gas (He) flow rate, injector temperature, and detector temperature were set as 1.2 mL min⁻¹, 240 °C, and 290 °C, respectively. The oven temperature program was as follows: initially 50 °C, increasing at 3 °C/min to 80 °C, then at 35 °C/min to 120 °C, and held for 2 min. Under these conditions, the retention times for *cis*-1,3-D, MITC, CP, and *trans*-1,3-D were 7.9, 9.0, 9.1, and 9.3 min, respectively.

Results and Discussion

Existence of Persistent Soil Fumigant Residues. After incubation with ≥ 1000 mg kg⁻¹ fumigants for 30 d, soils were evaporated in a thin layer for 20 h, and extracted with ethyl acetate at 20 °C for 24 h. Target fumigants were detected in all extracts, and the content was significant. In Arlington, Glenelg, and Hagerstown soil, contents of residual 1,3-D were 2.03 ± 0.14, 4.27 ± 0.37, and 12.54 ± 0.69 mg kg⁻¹, respectively; contents of residual CP were 7.68 ± 0.46, 10.55 ± 1.45, and 46.87 ± 0.50 mg kg⁻¹, respectively; and contents of residual MITC were 2.98 ± 0.03, 3.51 ± 0.17, and 5.13 ± 0.04 mg kg⁻¹, respectively. With the same incubation and extraction procedures, no residues were found either in soil samples

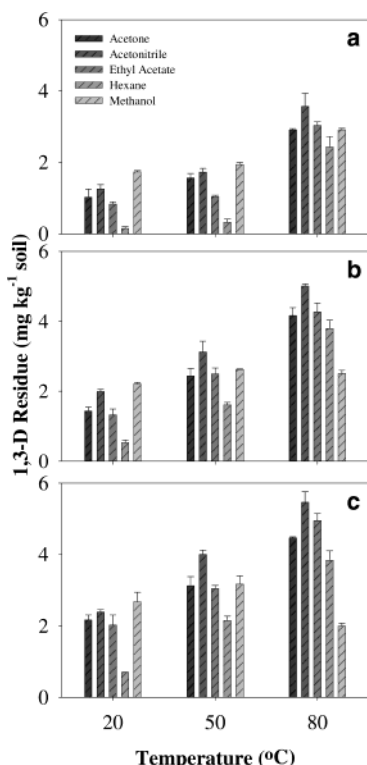


FIGURE 1. Extracted 1,3-D residues from 5% Florida organic soil-amended Arlington soil by different solvents at different temperature for (a) 1, (b) 12, and (c) 24 h. Error bars represent standard deviations of triplicate samples.

without pesticide spiking or in control vials (containing no soils) with similar fumigant spiking. Evidently, formation of persistent soil fumigant residues is significant, and a portion of applied fumigants may be retained in soils that is resistant to degradation and evaporation.

Extraction Method Optimization. Fumigant-incubated and evaporated soils were extracted under different conditions. The extraction efficiency varied with solvent, extraction time, and temperature. At 20 °C, methanol was the most effective extracting solvent and hexane was the least efficient. The extraction efficiency of the five solvents followed this order: methanol > acetonitrile > acetone > ethyl acetate > hexane (Figure 1). At 50 °C, methanol was still the most efficient extractant with an extraction duration of 1 h, but acetonitrile became more efficient if the extraction time was extended to 12 h or longer. At 80 °C, regardless of the extraction duration, acetonitrile had the highest extraction rate (Figure 1). In general, the extraction efficiency increased with extraction time and temperature. For example, when the incubated soil was extracted with methanol at 20 °C for 1, 12, and 24 h, recovery of 1,3-D was 1.74 ± 0.03 , 2.21 ± 0.04 , and 2.68 ± 0.27 mg kg⁻¹, respectively. When samples were extracted with acetonitrile for 24 h at 20, 50, and 80 °C, the corresponding values were 2.39 ± 0.06 , 4.01 ± 0.12 , and 5.46 ± 0.25 mg kg⁻¹, respectively (Figure 1). Apparently, extraction with acetonitrile at 80 °C for 24 h was the most effective method tested to recover persistent soil fumigant residues. Under these conditions, extending the extraction time from 24 to 48 h did not increase fumigant recoveries, suggesting that extraction is complete within 24 h. If the residue recovery under this extraction condition is considered to be 100%, the recovered 1,3-D, CP, and MITC by ethyl acetate extraction at 20 °C for 24 h were merely 37%, 65%, and 38%, respectively. Obviously, routine methods such as extracting soil with ethyl acetate at 20 °C for 1 h are not competent for persistent fumigant residue extraction.

TABLE 2. Persistent Soil Fumigant Residues Extracted with Acetonitrile at 80 °C for 24 h^a

soil	1,3-D (mg (kg of soil) ⁻¹)	CP (mg (kg of soil) ⁻¹)	MITC (mg (kg of soil) ⁻¹)
Arlington	5.4 (0.5)	11.8 (0.9)	8.3 (0.1)
Glenelg	9.5 (0.4)	26.9 (0.2)	14.3 (0.4)
Hagerstown	21.7 (0.5)	66.9 (3.2)	18.5 (1.9)

^a Data are means of triplicates, and values in parentheses are standard errors.

Sawhney et al. (11) proposed a method to extract persistent residues of volatile organic compounds such as EDB from soil by extraction with methanol (1:5 mass/volume ratio) at 75 °C for 24 h in a sealed vial. Nevertheless, the authors pointed out that acetone and acetonitrile were more efficient extraction solvents with respectively 121% and 122% of extracted EDB relative to methanol extraction under the described conditions. In the present case, we found that methanol or acetone was not as efficient as acetonitrile in extracting fumigant residues. At 80 °C for 24 h, 1,3-D, CP, and MITC extracted from the incubated soils by methanol were only 37%, 45%, and 57% of that extracted by acetonitrile, respectively; residues extracted by acetone were approximately 82%, 69%, and 80% of that extracted by acetonitrile, respectively. The higher extraction efficiency of acetonitrile (unlimited water-miscible and commonly used as nonaqueous titration media) is likely due to its greater polarity and smaller molecular size. It is also noteworthy that 1,3-D reacts slowly with methanol at high temperature. At 80 °C for 1, 12, and 24 h, the 1,3-D extracted by methanol was 2.91 ± 0.04 , 2.51 ± 0.08 , and 2.01 ± 0.07 mg kg⁻¹, respectively, decreasing as the extraction time increased. Accompanying the recovery decrease, an increase of the product 3-chloroallyl alcohol was observed (data not shown).

Given the large volume of solvent required to extract soil at 1:5 mass/volume ratio as proposed by Sawhney et al. (11), different soil/solvent ratios were also tested in this study. At 80 °C for 24 h, extraction of soil with acetonitrile at 1:1, 1:2, and 1:5 soil/solvent ratios gave equivalent fumigant recoveries (data not shown), indicating that a 1:1 ratio is adequate. Further, after the initial 1:1 ratio extraction, soils were washed three times with acetonitrile (5 mL each time) and then extracted again with 5 mL of the solvent at 80 °C for 24 h. Little 1,3-D was detected in the second-round extracts, demonstrating that the first extraction was complete. Clearly, of the methods included in this study, extraction with acetonitrile in sealed vials at 80 °C and 1:1 soil/solvent ratio for 24 h was the most efficient method to recover persistent soil fumigant residues.

Formation of Persistent Soil Fumigant Residues. The formation of persistent fumigant residues in soil was investigated by incubating soils under different conditions. Extraction of the residues was conducted with the optimized method. Fumigants (1,3-D, CP, and MITC) incubated individually with soils (10% moisture content) at 20 °C for 30 d formed significant contents of residues, and the content varied with soil types and fumigant properties (Table 2). Overall, there were 0.4–4% of the applied fumigants retained as persistent residues in soil. Considering the nonionic, volatile, and weakly sorptive properties of fumigants, the persistent residues must be retained in soil by mechanisms other than physical attraction. It is suggested that molecular diffusion into the matrix is a major reason for retention of weakly sorbing nonpolar compounds in soil (13) and micropores in soil aggregates may be responsible for the retention (3). The test soils demonstrated comparative capacities for fumigant entrapment: Hagerstown > Glenelg > Arlington (Table 2), following the same order as the silt

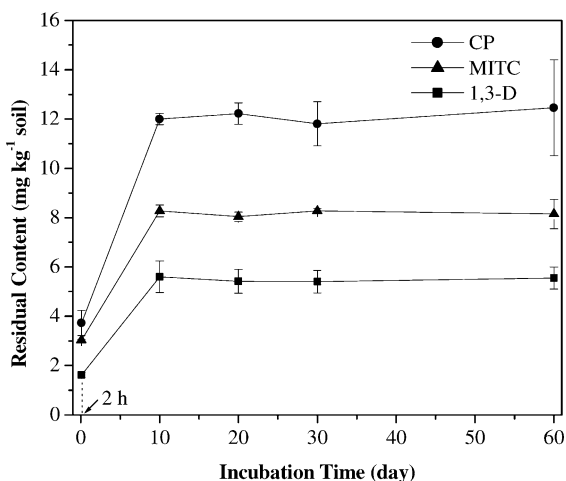


FIGURE 2. Fumigant residues in Arlington soil with different incubation durations. Error bars represent standard deviations of triplicate samples.

content (Table 1). During the development of soil aggregates, bundles of clay flocs (ultimate structural units) attach themselves to, and sometimes engulf, silt and sand particles (14). Indeed, silt particles play an important role in soil aggregate formation and stability (15). With a certain amount of cements such as clay and humic substances, silt particles may decide the development of soil aggregates and micropores in which fumigant residues are retained.

Release of persistent soil fumigant residues through volatilization is fairly slow. Persistent residues of 1,3-D, CP, and MITC in Arlington soil (incubated with a mixture of 1,3-D, CP, and MITC, each at 100–169 mg kg⁻¹) evaporated for 20 h were 1.05 ± 0.07 , 0.15 ± 0.03 , and 0.90 ± 0.04 mg kg⁻¹, respectively. Extension of the evaporation time to 120 h resulted in only a small decrease in residues, and the measured values were 0.96 ± 0.02 , 0.11 ± 0.00 , and 0.84 ± 0.02 mg kg⁻¹, respectively. Steinberg et al. (3) estimated that half-equilibrium time of the residual EDB in a 1:2 soil–water suspension was 20–30 yr at 25 °C. Soil micropores that retain fumigants are tortuous and irregularly shaped, and it is difficult for entrapped molecules to dissipate out. Moreover, such micropores may not be accessible to microorganisms. Consequently, persistent soil EDB residue was resistant to indigenous microbes and remained in soils for over 19 yr after field application (3).

Formation of persistent soil fumigant residues is a relatively rapid process. Even when the incubation time was as short as 2 h, noticeable contents of persistent fumigant residues were generated. The residues increased with incubation time and maximized within 10 d, with little change with increasing time (Figure 2). Evidently, the diffusion process began immediately following fumigant spiking and continued until apparent equilibrium, after which no additional residues were captured.

Effect of Application Rate. At an application rate of 24 mg (kg of soil)⁻¹ (level 1, Table 3), the persistent 1,3-D residue in Arlington soil was 0.37 ± 0.04 mg kg⁻¹, equivalent to 36% and 7% of those formed at 119 (level 2, Table 3) and 1190 mg kg⁻¹ (level 3, Table 3) application rates, respectively. For other fumigants and in other soils, similar phenomena were observed (Table 3). Clearly, the content of persistent residue formed in soil increased with fumigant application rate. Diffusion is driven by concentration gradient. At higher application rates, more fumigants diffused and were entrapped in soil micropores, resulting in greater residue formation. In sealed vials with moist soils, fumigants may undergo chemical and biological degradation; thus, persistent residues may not be proportional to the application rate. For

TABLE 3. Persistent Fumigant Residues in Arlington Soil with Different Application Rates^a

application rate ^b	1,3-D (mg (kg of soil) ⁻¹)	CP (mg (kg of soil) ⁻¹)	MITC (mg (kg of soil) ⁻¹)
level 1	0.4 (0.0)	0.1 (0.0)	0.4 (0.1)
level 2	1.0 (0.1)	1.1 (0.3)	2.2 (0.3)
level 3	5.4 (0.5)	11.8 (0.9)	8.3 (0.1)

^a Data are means of triplicates, and values in parentheses are standard errors. ^b Levels 1–3 are 24, 119, and 1190 mg (kg of soil)⁻¹ for 1,3-D; 34, 169, and 1690 mg (kg of soil)⁻¹ for CP; and 10, 100, and 1000 mg (kg of soil)⁻¹ for MITC, respectively.

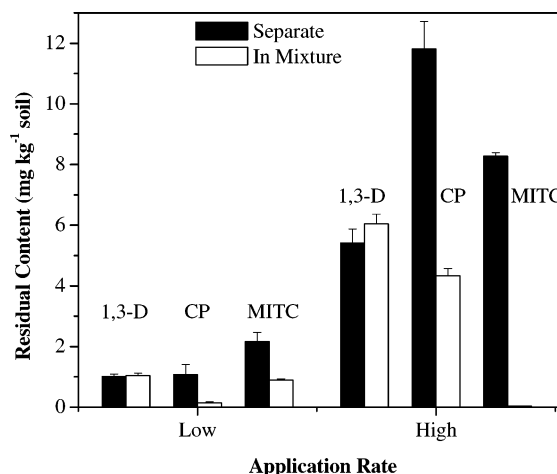


FIGURE 3. Residues of fumigants applied separately and in mixture in Arlington soil. Low and high application rates are 119 and 1190 mg (kg of soil)⁻¹ for 1,3-D, 169 and 1690 mg (kg of soil)⁻¹ for CP, and 100 and 1000 mg (kg of soil)⁻¹ for MITC, respectively. Error bars represent standard deviations of triplicate samples.

example, at application rates of 10, 100, and 1000 mg kg⁻¹, persistent MITC residues formed in the Arlington soil accounted for 3.6%, 2.2%, and 0.8% of the applied amounts, respectively. Approximately 0.7% of the applied CP at 1690 mg kg⁻¹ retained in the soil as persistent residues, while the percentage decreased to 0.2% when the application rate was reduced to 34 mg kg⁻¹ (Table 3). In sandy loam soil, CP is easily degradable with a half-life of 8–24 h (16). At a low application rate, most of the applied CP would be degraded prior to diffusing into soil micropores.

Effect of Coexisting Fumigants. When fumigants were spiked separately or in mixture, persistent residues in soil varied. For instance, when 1,3-D, CP, and MITC were applied in Arlington soil individually at 100–169 mg kg⁻¹, measured persistent residues were 1.02 ± 0.07 , 1.08 ± 0.33 , and 2.17 ± 0.30 mg kg⁻¹, respectively. While the three chemicals were spiked as a mixture (each at the original rate), residual 1,3-D increased slightly, and residual CP and MITC decreased significantly (low application rate, Figure 3). Similar trends occurred at higher application rates (Figure 3). Evidently, coexisting fumigants interact with one another in soil-persistent residue formation. The data suggest that soil micropores are limited and that fumigants compete for the space. 1,3-D has the preference over CP and MITC to the retention sites, seemingly due to its higher volatility.

Effect of Temperature. Formation of persistent fumigant residues at different temperatures was tested. For 1,3-D and MITC, residues increased as incubation temperature rose from 20 to 35 °C and decreased as temperature rose to 50 °C (Figure 4). For CP, residues decreased as temperature increased (Figure 4). The rate of fumigant degradation in moist soil is enhanced as temperature increases (17–19), and sorption is decreased (20, 21). On the other hand,

TABLE 4. Persistent Residues of Fumigants in Soils after Organic Matter Removal^a

fumigant ^b	Arlington		Glenelg		Hagerstown	
	original ^c	OMR ^d	original	OMR	original	OMR
1,3-D (mg (kg of soil) ⁻¹)	5.4 (0.5)	2.2 (0.1)	8.3 (0.4)	3.3 (0.1)	21.7 (0.5)	2.6 (0.2)
CP (mg (kg of soil) ⁻¹)	11.8 (0.9)	0.1 (0.0)	19.9 (0.2)	0.6 (0.0)	66.9 (3.2)	0.8 (0.1)
MITC (mg (kg of soil) ⁻¹)	8.3 (0.1)	5.2 (0.3)	14.3 (0.4)	4.1 (0.1)	18.5 (1.9)	2.6 (0.1)

^a Data are means of triplicates, and values in parentheses are standard errors. ^b Application rates for 1,3-D, CP, and MITC are 1190, 1690, and 1000 mg kg⁻¹, respectively. ^c 10% moisturized soil without organic matter removal. ^d 10% moisturized soil with organic matter removed.

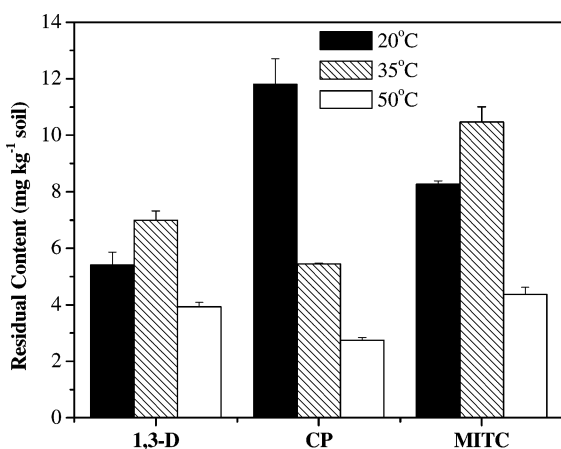


FIGURE 4. Fumigant residues in Arlington soil under different incubation temperature. Error bars represent standard deviations of triplicate samples.

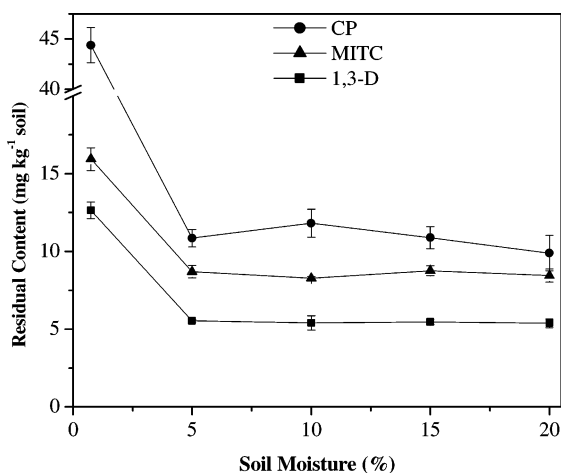


FIGURE 5. Fumigant residues in Arlington soil with different moisture contents. Error bars represent standard deviations of triplicate samples.

increased temperature may promote molecular diffusion of fumigants into soil micropores. The extent to which temperature influences these processes is uncertain. As a result, fumigant-specific responses to temperature are observed in persistent residue formation in soil.

Effect of Moisture. Fumigants (1000–1690 mg kg⁻¹) incubated with air-dried Arlington soil (0.75% moisture content) at 20 °C for 30 d formed 1,3-D, CP, and MITC residues at 12.64 ± 0.54 , 44.38 ± 1.75 , and 15.94 ± 0.73 mg kg⁻¹, respectively. When soil moisture was adjusted to 5%, the respective residues decreased greatly to 5.53 ± 0.11 , 10.85 ± 0.57 , and 8.69 ± 0.40 mg kg⁻¹. With continued increase in soil moisture to 20%, the corresponding residues showed little change (Figure 5). Evidently, soil moisture content is an essential factor that determines persistent fumigant residue formation. It has been reported that with an increase in soil

moisture content, the rate of 1,3-D degradation increased, CP degradation was not affected, and MITC degradation was inhibited (17, 18). Adsorption of fumigants on soil (evaluated by batch methods) decreased as the soil moisture content increased (21). Nevertheless, impacts of moisture on formation of persistent soil fumigant residues were distinct from those on fumigant degradation and adsorption. It is speculated that most micropores in the air-dried soil were empty, allowing fumigant molecules to diffuse in. At 5% moisture or higher, the majority of soil micropores were occupied or shielded by water, and diffusion of the spiked chemicals into the micropores was decreased. Applying fumigants to moist soil may decrease formation of persistent fumigant residues.

Effect of Organic Matter. The content of persistent fumigant residues decreased dramatically after soil organic matter (SOM) was removed. For example, persistent residues of 1,3-D, CP, and MITC in Hagerstown soil were reduced 88%, 99%, and 86%, respectively, after removal of indigenous OM by combustion (Table 4). Fumigant degradation is greater in soils rich in OM (22, 23), and total residual fumigants would be expected to increase after removal of SOM because of slower degradation. As a matter of fact, persistent fumigant residues decreased after SOM was removed, strengthening our contention that this portion of fumigants is not subject to degradation. It is known that OM functions as a major cement in soil aggregate formation (14). The OM removal dispersed soil aggregates and destroyed intra-aggregate micropores that may have retained fumigant residues.

The Arlington soil exhibited little change in persistent 1,3-D, CP, and MITC residue retention (data not shown) after amendment with 3% and 6% of the Florida organic soil. Even in 100% of the organic soil, measured persistent residues of 1,3-D, CP, and MITC were respectively 3.08 ± 0.39 , 0.78 ± 0.25 , and 1.29 ± 0.07 mg kg⁻¹, much smaller than in the mineral soils. Organic matter may retain fumigants through physical adsorption and matrix entrapment (22, 24). The fact that external OM addition did not increase persistent soil fumigant residues suggests that this portion of fumigants is not associated directly with SOM and the only place in soil for the residue retention is micropores. Presumably, the OM amendment did not increase soil micropores, which are products of soil aggregate development. As a result, the organic amendment had little influence on the formation of persistent fumigant residues. It may be inferred that well-humified organic matter with a dense texture such as the Florida organic soil and most SOM does not have the ability to retain persistent fumigant residues. This is also strengthened by the fact that Hagerstown soil retained much more persistent fumigant residues than Glenelg soil (Table 2), while the former contained less organic matter (Table 1). Pignatello (9) postulated that diffusion into the organic matter matrix was the major reason for halocarbon retention in soil, on the basis of the fact that the residues correlated with organic carbon contents in whole soils and soils pretreated with H₂O₂. Our data suggested that only organic matter that participates in soil aggregation contribute to fumigant entrapment.

Effect of Soil Aggregation. When 1,3-D (1190 mg kg⁻¹) was incubated with 10% moisturized coarse (1–2 mm),

medium (0.1–0.25 mm), and fine (<0.075 mm) quartz sand for 30 d, extracted persistent residues were ND (nondetectable), ND, and $0.16 \pm 0.01 \text{ mg kg}^{-1}$, respectively. A small amount of fumigants may have been retained on fine particles via enthalpy adsorption, following a similar mechanism as hygroscopic water. In montmorillonite (specific surface area (SSA) $7.5 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$), kaolinite (SSA $3.6 \times 10^4 \text{ m}^2 \text{ kg}^{-1}$), and hematite (SSA $1.6 \times 10^4 \text{ m}^2 \text{ kg}^{-1}$), persistent 1,3-D residues were 1.32 ± 0.08 , 0.81 ± 0.18 , and $0.65 \pm 0.04 \text{ mg kg}^{-1}$, respectively: greater than in the fine sand yet much less than in Arlington soil (clay 7.4%, Table 1) incubated under similar conditions. Clearly, neither mineralogy nor particle size of soil is important in fumigant trapping. When the Arlington soil (<2 mm) was ground to <0.25 and <0.075 mm, adjusted to 10% moisture content, and incubated with 1,3-D at $1190 \text{ mg (kg of soil)}^{-1}$, the persistent residue decreased from 5.41 ± 0.46 to 2.99 ± 0.05 and $2.75 \pm 0.09 \text{ mg kg}^{-1}$, respectively, demonstrating the significance of soil aggregation in fumigant residue formation. Similarly, decrease of soil aggregation by pulverization greatly enhanced the release of residual EDB (3). Evidently, micropores within soil aggregates are major sites for persistent fumigant residue retention. Factors such as soil organic matter, clay particles, and silt content influence persistent fumigant residue formation by controlling soil aggregation. The pool in soil where persistent fumigant residues reside should be further investigated, and the leaching potential of the residues into groundwater warrants systematic assessment.

Acknowledgments

The authors thank Dow Agrosiences Co. (Indianapolis, IN) and Niklor Chemical Co. (Long Beach, CA) for their generous donation of 1,3-D and CP.

Literature Cited

- (1) Batzer, F. R.; Balcer, J. L.; Peterson, J. R.; Wolt, J. D. In *Fumigants: Environmental Fate, Exposure, and Analysis*; Seiber, J. N., et al., Eds.; ACS Symposium Series 652; American Chemical Society: Washington, DC, 1996; p 60.
- (2) Wilhelm, S. N.; Shepler, K.; Lawrence, L. J.; Lee, H. In *Fumigants: Environmental Fate, Exposure, and Analysis*; Seiber, J. N., et al., Eds.; ACS Symposium Series 652; American Chemical Society: Washington, DC, 1996; p 79.

- (3) Steinberg, S. M.; Pignatello, J. J.; Sawhney, B. L. *Environ. Sci. Technol.* **1987**, *21*, 1201.
- (4) Pignatello, J. J. *Environ. Toxicol. Chem.* **1990**, *9*, 1107.
- (5) Tao, T.; Maciel, G. E. *Environ. Sci. Technol.* **2002**, *36*, 603.
- (6) Parsons, D. W.; Witt, J. M. *Pesticides in Groundwater in the United States of America*; Oregon State University Extension Service: Corvallis, OR, 1989.
- (7) U.S. Environmental Protection Agency. *Drinking Water Contaminant Candidate List*; Federal Register 63 FR 10273; U.S. EPA: Washington, DC, 1998.
- (8) U.S. Geological Survey. *Pesticides in Surface and Ground Water of the United States*; USGS: Washington, DC, 1998.
- (9) Pignatello, J. J. *Environ. Toxicol. Chem.* **1990**, *9*, 1117.
- (10) Gan, J.; Yates, S. R.; Papiernik, S. K.; Crowley, D. *Environ. Sci. Technol.* **1998**, *32*, 3094.
- (11) Sawhney, B. L.; Pignatello, J. J.; Steinberg, S. M. *J. Environ. Qual.* **1988**, *17*, 149.
- (12) Ball, D. F. *J. Soil Sci.* **1964**, *15*, 84.
- (13) Pignatello, J. J. In *Reactions and Movement of Organic Chemicals in Soils*; Sawhney, B. L., Brown, K., Eds.; SSSA Special Publication 22; Soil Science Society of America: Madison, WI, 1989; p 45.
- (14) Hillel, D. *Environmental Soil Physics*; Academic Press: San Diego, CA, 1998; p 118.
- (15) Voronin, A. D.; Sereda, N. A. *Moscow Univ. Soil Sci. Bull.* **1976**, *31*, 100.
- (16) U.S. Environmental Protection Agency. *Pesticide Environmental Fate One Line Summary: Chloropicrin*; U.S. EPA Environmental Fate and Effects Division: Washington, DC, 1992.
- (17) Gan, J.; Papiernik, S. K.; Yates, S. R.; Jury, W. A. *J. Environ. Qual.* **1999**, *28*, 1436.
- (18) Gan, J.; Yates, S. R.; Ernst, F. F.; Jury, W. A. *J. Environ. Qual.* **2000**, *29*, 1391.
- (19) Smelt, J. H.; Leistra, M. *Pestic. Sci.* **1974**, *5*, 401.
- (20) Leistra, M. *J. Agric. Food Chem.* **1970**, *18*, 1124.
- (21) Tamagawa, S.; Irimajiri, T.; Oyamada, M. *Jpn. J. Agric. Pestic.* **1985**, *10*, 205.
- (22) Gerstl, Z.; Mingelgrin, U.; Yaron, B. *J. Soil Sci. Soc. Am.* **1977**, *41*, 545.
- (23) Gan, J.; Yates, S. R.; Crowley, D.; Becker, J. O. *J. Environ. Qual.* **1998**, *27*, 408.
- (24) Ashley, M. G.; Leigh, B. L.; Lloyd, L. S. *J. Sci. Food Agric.* **1963**, *14*, 153.

Received for review October 21, 2002. Revised manuscript received February 20, 2003. Accepted February 25, 2003.

ES0262535